

Operation of the Thermo QUANT'X X-Ray Fluorescence Spectrometer

1 Introduction

The Thermo QUANT'X is an energy dispersive x-ray fluorescence spectrometer (EDXRF) used for non-destructive compositional analysis of solids and liquids ranging in atomic number from sodium to uranium. The instrument can operate under an air, helium, or vacuum atmosphere.

2 Scope

This document applies to personnel using the associated instrument(s)/equipment in the following disciplines/categories of testing: general physical and chemical analysis in support of metallurgy, anthropology or general chemistry examinations. The operation of the Thermo QUANT'X X-ray Fluorescence Spectrometer will follow procedures defined in the current revision of Chemistry Unit (CU) Metallurgy standard operating procedure (SOP) *Compositional Analysis by X-ray Fluorescence Spectrometry (EDXRF)* and the specific parameters described below.

3 Principle

The Thermo QUANT'X uses a Rh-target x-ray tube to generate the incident x-ray beam and a Peltier-cooled, lithium-drifted silicon detector (PCD) to collect and measure photons emitted by the sample. These components are arranged in a bottom-up configuration so that specimens are placed face down over the stage portal for measurement. Elements with atomic number equal to and greater than 11 (sodium) can be measured. Measurements can be made in an air, vacuum, or helium environment. Instrument control and data analysis are performed using WinTrace software running on a personal computer that is connected to the analyzer.

4 Specimens

Any liquid or solid sample can be analyzed on this instrument, provided the cover can be closed. Larger specimens may have to be sectioned to provide access to an area of interest to be analyzed. Although the stage portal is approximately 1 inch in diameter, the portal does not have to be completely covered for qualitative measurement. Typically, a few grams of liquid or solid will provide satisfactory results. If quantitative results are desired, it is necessary to prepare the samples so that they have a flat, smooth surface. In the case of fine powder or liquid samples, the thin support film (e.g., 2.5 μm Mylar) used to contain the sample provides the required surface.

5 Equipment/Materials/Reagents

- a. ThermoScientific ARL QUANT'X EDXRF Energy Dispersive X-Ray Fluorescence Spectrometer
- b. Calibration standard(s) such as "Thermo OFHC" or a copper Certified Reference Material (CRM), purity $\geq 99\%$ Cu
- c. CRMs of alloys similar to the type(s) under analysis, if elemental quantitation is required or limit of detection (LOD) is being established
- d. One inch diameter (or larger) plastic sample cups
- e. Chemplex X-Ray Mylar (2.5 μm thick) or polypropylene film (6.3 μm thick) or similar
- f. Helium gas, purity $\geq 99.95\%$ He, optional
- g. "Excitation Filter Guide" chart, provided by ThermoScientific

6 Standards and Controls

The instrument performance check (energy adjustment routine) requires a pure copper disc. Normally, the Thermo OFHC standard is used for this procedure, but any CRM pure copper disc is adequate for this purpose. For quantitation, alloy class comparison or to establish the absence of an element, CRMs as similar as possible to the material under analysis are used.

The energy adjustment routine is used to fine tune the signal processor. Initiation of the automated routine is described in 8.1 Basic Operation below. In the event the energy adjustment is unsuccessful, the routine should be rerun. If repeated failure of the energy adjustment routine occurs and the operator cannot correct the problem, then the instrument must be serviced. The instrument is fine-tuned each day prior to being used for casework. One copy of the Energy Adjustment Report is kept with the instrument and one copy with the applicable case notes.

For quantitative analysis, a calibration curve is generated for each analyte (element) to be quantified. The calibration curve(s) are matrix-dependent and so must be developed from materials as similar as possible to the matrix of the unknown sample.

7 Sampling

If large numbers of physically indistinguishable samples are received for compositional analysis, a sampling plan may be employed for testing. If the sampling plan will be used to make an inference about the population, then the plan will be based on a statistically valid approach. All of the samples may be tested at the examiner's discretion. Any sampling plan and corresponding

procedure used will be recorded in case notes.

8 Procedure

8.1 Basic Operation

The basic operation from a powered-down condition consists of the following steps.

- a. Turn on computer and instrument. From a cold start, the red “Detector” light on the front of the instrument will blink until the detector is cooled sufficiently to operate.
- b. Position the Thermo OFHC or other pure copper disc for analysis.
- c. In the WinTrace software, select the “Energy Adjustment Shortcut” from the desktop or open Acquisitions Manager and select “Analyze” > “Energy Adjustment”.
- d. The energy adjustment routine normally uses the parameters listed in Table 1. Three acquisition rates (AR) are available. The energy adjustment must be run at the AR to be used for acquiring the spectrum from the unknown, typically Medium.

Table 1: Typical Operating Parameters for Energy Adjustment Routine

<u>Parameter</u>	<u>Value</u>
Line Energy	8.041 keV
Filter	Pd Medium
Voltage	20 kV
Current	Auto
Acquisition Range	40 keV
Acquisition Rate	Medium
Spinner	OFF

- e. Select “OK” to start the energy adjustment routine. The software self-adjusts the current to achieve an appropriate dead time of 30-59%.
- f. Upon successful completion, the Energy Adjustment Report appears with diagnostic information. The results of the energy adjustment (pass/fail) will be recorded in the instrument log accompanying the instrument. The report will be retained in the logbook for system performance diagnostics.
- g. The report will be compared to previous energy adjustment results:
New and old Gain DAC settings should change by no more than 100 on a weekly basis.
1) FWHM should not exceed 195 eV for the pure copper disc measured at the medium AR with the PCD detector.

- 2) Counts (cps/mA): This indicator of x-ray tube performance should be compared with previous values. Significant changes might be a sign of normal x-ray tube aging or of stability problems.

If any of the above conditions is unacceptable, consult a service representative.

- h. If the energy adjustment is unsuccessful, the routine will be performed again. If repeated failure of the energy adjustment occurs and the operator cannot correct the problem, the instrument must be serviced.

8.2 General Analysis

- a. Place the specimen on the stage face down over the stage portal. The surface to be analyzed should be flush with the stage surface, although the portal need not be completely covered for qualitative analysis. Center the area to be analyzed over the center of the hole. No part of the specimen should ever protrude down into the portal.
- b. Program the run by opening a qualitative or quantitative “tray list” (8.3 Qualitative Analysis or 8.4 Quantitative Analysis) and selecting the parameters for each sample and condition to be run.
 - i. To run one specimen at multiple analysis conditions, enter the identical specimen ID on additional lines, selecting the new desired condition for each.
 - ii. To measure multiple specimens under the same analysis condition, enter the different specimen IDs on each line, selecting the same condition. Altering a condition that appears more than once in a tray list will alter all instances of that condition. As the analysis proceeds, the instrument will prompt for the required sample change.
 - iii. Define each operating condition. Optimum x-ray tube voltage(s) and mode of irradiation (filter type or unfiltered) depend on the sample composition and the objective of the analysis. Combinations that typically generate good intensities for specific elements are suggested on the “Excitation Filter Guide” provided by the manufacturer. However, since matrix interactions can be severe, the choice of the optimal conditions for a given analysis may deviate from these recommendations. The tube current is dictated primarily by the need to have a sufficient count rate to collect a spectrum, corresponding to deadtime of ~50% (30-59%), and is automatically adjusted by the instrument control software.
 - iv. Select the appropriate measurement atmospheric condition: air, helium, or vacuum. (Air is the default setting for each standard condition.)
- c. Identify the peaks present in the spectrum using the WinTrace Spectrum Viewer program. The Auto Peak Identification routine is activated by the thumbprint icon.

Software-generated identifications must be interpreted by an experienced operator to prevent misidentification of peaks. The “MLK” function overlays sets of characteristic emission lines on the spectrum to aid in x-ray peak identification. The interactive periodic table (found under “Tools” > “Peak Identification” > “Setup”) can be used to adjust the sensitivity of the labeling routine and to force or remove element labels. Double-clicking on an element label on the spectrum display will remove an individual peak label without blocking the entire line series for that element. Refer to CU Metallurgy SOP Manual *Compositional Analysis by EDXRF* for more details regarding peak identification.

8.3 Qualitative Analysis

- a. Spectra for qualitative analysis are collected in WinTrace “Acquisitions Manager” using a Qualitative Tray List. Before acquisition, be sure to specify the location the spectra will be saved by selecting “Edit” > “Spectrum Location”.
- b. Open a Qualitative Tray List; enter the sample ID; select filter conditions then click off of the row for that sample. Click back onto the sample row and select the “Edit Conditions” icon to change the acquisition settings and environment if desired.
- c. To begin acquisition, select the “Go” icon.
- d. After data collection, the x-ray tube automatically powers down. The Peltier detector requires electricity for cooling. As long as the instrument remains plugged in, power is applied to the cooling circuit, even if the power switch is turned off.
- e. Use the Auto Peak Identification (thumbprint) and “MLK” icons to aid in x-ray peak identification. Hold down the Control key and press an Arrow key, ← or → , to change the element for which the MLK lines are shown.
- f. Spectra can be viewed, annotated, and overlaid in the WinTrace “Spectrum Viewer” application.
- g. A copy of the spectrum, with peaks labeled and acquisition conditions listed, will be retained in the case notes.

8.4 Quantitative Analysis

8.4.1 Method Development

Quantitative evaluation of spectra requires acquisition of the unknown spectra, acquisition of CRM calibration standards, acquisition of peak profiles for pure elements and selection of a mode of analysis that will be conducted in WinTrace “Method Explorer”.

- a. Determine favorable analysis conditions for each element of interest empirically by running qualitative analyses and/or by using the “Excitation Filter Guide”.

- b. Pure element peak profiles are collected in WinTrace “Acquisitions Manager” using a Reference Tray List. Before acquisition, be sure to specify the location the spectra will be saved by selecting “Edit” > “Spectrum Location”. These spectra will later be imported into the chosen Method. If “L” series spectral lines are of interest for quantitation, the conditions for acquisition of pure element peak profiles must be identical to those used to collect the unknown spectra. If only “K” series spectral lines will be analyzed, the acquisition conditions need not match.
- c. CRM spectra can be collected in WinTrace “Acquisitions Manager” using a Reference Tray List or can be collected directly into the Method developed for analysis. If collecting in “Acquisitions Manager”, before acquisition be sure to specify the location the spectra will be saved by selecting “Edit” > “Spectrum Location”. These spectra will later be imported into the chosen Method.
- d. Spectra for quantitative analysis can be collected in WinTrace “Acquisitions Manager” using a Quantitative Tray List or can be collected directly into the Method developed for analysis. Before acquisition, be sure to specify the location the spectra will be saved by selecting “Edit” > “Spectrum Location”. These spectra will later be imported into the chosen Method.

8.4.2 Analysis

The instrument software “Method Explorer” contains analysis techniques for semi-quantitative and quantitative analysis. Two of these are described briefly below. Select the analysis technique by selecting “File” > “Settings”.

- a. “Fundamentals Parameters (alpha)” is a fundamental parameters-based quantitation routine. This technique requires only a limited number of standards to generate calibration curves for the analytes of interest. It provides quantitative analysis over a wide range of concentrations and can be used with standards that are dissimilar from the unknown samples. The resulting calculated concentrations can be viewed as absolute or normalized values.
- b. “Intensity Correction” is an empirical technique that uses a suite of calibration standards to generate calibration curves. The standards must be similar in matrix to the unknown in order to account for matrix interactions. This analysis requires that the standards bracket the compositions of the analytes of interest in the unknown.
- c. Each analysis technique offers different options for spectrum processing. Typically, “Force through zero” should be selected (compensation for background is included in the software routine). The default setting for spectrum processing for Fundamental Parameters – Alpha is “XML” for every element. If a large peak dwarfs a smaller adjacent peak, setting the spectrum processing mode for the element with the larger peak to “Derivative” can improve the analysis of the smaller peak.

- d. Once all of the data are entered, the spectra are collected and the analysis parameters are chosen, select “Calibrate”, then select a sample list to “Analyze”. Results from the calibration and analysis are saved in the Method. These results can be exported in .csv format to a database program like Excel for statistical evaluation. If quantitative data are to be reported, the “Calibration” and “Analysis” reports will be retained in validation records and in the case file.

9 Instrumental Conditions

- a. The “Excitation Filter Guide” chart, provided by ThermoScientific, contains recommendations for analysis conditions that have been found to be useful for the preliminary screening of materials. If the specimen is a liquid sample or a vacuum sensitive material, choose a helium or air atmosphere as appropriate to the samples and the analysis objectives. Instrumental conditions can be adjusted at the discretion of the analyst to optimize the analyses.
- b. Acquisition times will depend on the conditions chosen and the sample area exposed to the incident beam to acquire sufficient counts for analysis.
- c. Two x-ray collimators are available, 1.0 mm and 8.8 mm. These are used to limit the x-ray beam size incident on the sample. For routine operation, the 8.8 mm filter wheel collimator is typically used.
- c. Three acquisition rates are available: Low, Medium, and High. The Medium rate normally provides sufficient resolution for qualitative or quantitative analysis. If the Low or High rate is preferred for a particular analysis, the Energy Adjustment routine must be run for the appropriate acquisition rate.

10 Decision Criteria

10.1 Instrument Performance

Energy adjustment of the instrument will be undertaken whenever the measured x-ray peak positions differ by more than 0.05 keV from their theoretical positions.

10.2 Spectral Analysis

General decision criteria for peak identification, spectral comparison and quantitative EDXRF analysis are described in *Compositional Analysis by EDXRF*. Additional considerations particular to this instrument are:

- a. The Thermo QUANT’X EDXRF generates a low intensity system peak at the energy of

aluminum $K\alpha$ that interferes with identifying minor amounts of aluminum in alloys.

- b. The on-board peak identification software does not present marker lines for escape peaks* or sum peaks. This requires the operator to calculate and identify these peaks associated with the major constituents of a sample. (*Labels generated by the peak ID routine can identify the general vicinity of escape peaks.)

11 Calculations

In dilute solutions, the measured x-ray intensity of a particular element is typically directly proportional to its concentration in solution. If several samples of differing concentrations are analyzed to create a calibration curve, a standard linear regression analysis can be used to calculate the best fit line to the data. Typically, such a curve can be established using four solutions with known concentrations of the element of interest and a matrix blank containing below the level of detection of the element of interest. Concentrations of unknown samples are then determined by reference to the linear fit of the data.

12 Measurement Uncertainty

Typically, the Thermo QUANT'X is not used for quantitative analysis. Should it be required, the measurement uncertainty will be estimated in accordance with *Chemistry Unit Procedures for Estimating Measurement Uncertainty* in the CU Quality Assurance and Operations Manual.

13 Limitations

Compositional Analysis by EDXRF contains general limitations of compositional measurement by x-ray fluorescence spectrometry.

Samples of adequate size (usually a few grams) are required for optimal results. Where only smaller samples are available, the use of a microspot EDXRF is recommended.

14 Safety

- a. The ThermoScientific QUANT'X produces x-rays. Wear an x-ray film badge or dosimeter when operating this instrument. The instrument has a protective enclosure with internal safety interlocks to prevent inadvertent x-ray radiation exposure. Never bypass or disable the safety interlocks on this instrument.
- b. The detector and tube windows are comprised of beryllium and are extremely delicate. In the event of damage to a window, the beryllium dust created could pose an acute

health hazard. If this occurs, seal the chamber and seek assistance from the Laboratory Health and Safety Group.

15 References

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Buhrke, V.E., Jenkins, R., Smith, D.K., *Preparation of Specimens for X-ray Fluorescence and X-ray Diffraction Analysis*, Wiley-VCH, New York 1998

Tertian, R. and Claisse, F., *Principles of Quantitative X-Ray Fluorescence Analysis*, John Wiley & Sons, Inc. West Sussex, England 1982

Margui, E. and Van Grieken, R., *X-Ray Fluorescence Spectrometry and Related Techniques*, Momentum Press LLC, New York 2013

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Compositional Analysis by Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF), CU Metallurgy SOP Manual, latest revision

FBI Laboratory Quality Assurance Manual, Federal Bureau of Investigation, Laboratory Division, latest revision

FBI Laboratory Operations Manual, Federal Bureau of Investigation, Laboratory Division, latest revision

Rev. #	Issue Date	History
3	12/23/2015	Helium designated as optional in section 5.f. Operating parameter corrected in section 9.1.d. Peak labeling instruction added to section 9.2.c. Reorganized section 12 to make calibration curve procedure applicable to both liquid solutions and alloys. Editorially revised to clarify instructions throughout.
4	03/02/18	Renumbered Metallurgy SOP Manual documents. This document was formerly Metal 20 and is now designated Metal 501. Added personnel to section 2. Made minor editorial corrections throughout document. Clarified application in section 5.c. Incorporated section 7 into section 6 and renumbered subsequent sections. Added requirement for sampling plan retention in section 7. Removed reference to check sample in section 8.4.2.b, since verification requirements are addressed during method validation. Clarified definition in section 11. Updated safety requirements in section 14. Added additional references to section 15.

Approval

Redacted - Signatures on File

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